

Early Days*

BY W. L. BRAGG

It is now nearly sixty years since von Laue, Friedrich and Knipping made the discovery of X-ray diffraction by crystals. The story of 1911–1912 has often been told; how Ewald consulted von Laue about his Ph.D. dissertation on the double refraction of light based on the retarded potentials of waves scattered by the atoms arranged in a space lattice, which had been suggested as a subject by Sommerfeld; of how von Laue had his attention directed for the first time to the existence of such a fundamental feature as a space lattice, which had never been mentioned in the lectures at Göttingen on mineralogy which he had attended; of how he suggested to Ewald that it would be interesting to calculate what would happen if the wavelength were of the same order as the crystal spacing; of how he stimulated Friedrich to try the experiment with X-rays, although Sommerfeld discouraged such a dubious venture as an interference with Friedrich's regular research; of how Friedrich tried the experiment with his assistant Knipping, by testing whether a crystal of copper sulphate diffracted backwards an X-ray beam, and failed to find any effect; of how Knipping, when they were about to give up, tried as a wild shot putting the plate behind the crystal; and how he got the famous picture of diffracted spots which started X-ray crystallography.

My father was intensely interested in von Laue's results because at the time he upheld the theory that X-rays were a type of corpuscular radiation, the 'neutral pair' theory. This theory was not so strange as might appear. He had been led to it by deducing what we now know to be true, that when X-rays ionize a gas the energy is handed over to individual electrons here and there in the gas, as if they had been struck by a projectile. It must be remembered that this was before the days of the Wilson cloud chamber, and before the dual wave and particle nature of radiation had become a familiar idea. We had many discussions about the results in the summer holiday of 1912, and when I went back to Cambridge as a research student in the autumn I pored over von Laue's pictures. Here again chance played a part. It must be difficult nowadays to imagine how utterly ignorant physicists were at that time of the geometry of three-dimensional patterns. I happened to know about it, because Pope & Barlow had proposed a valency-volume theory of crystal

structure which although incorrect was highly suggestive, and a member of a small scientific society to which I belonged had given a paper on this theory. It brought home to me the fact that atoms in space lattices were arranged in planes! J.J. Thomson had been talking about the pulse theory of X-rays and, to cut a long story short, I explained von Laue's results as being due to the reflexion of a band of 'white' radiation by the planes of the crystal. I published a note (Bragg, 1912) showing the reflexion of X-rays by a mica sheet at a series of angles. Further, I showed that the spots von Laue had obtained with zincblende were characteristic of a face-centred cubic crystal, having heard about such a lattice by studying Pope & Barlow's papers (Bragg, 1913). Pope was intensely interested and encouraged me to try Laue photographs of NaCl and KCl, in which he also believed the atoms to be in the close packing of a face-centred cubic lattice. These photographs established the structure of the sodium chloride group of crystals (NaCl, KCl, KBr, KI).

This tentative start of crystal analysis, however, was soon completely superseded by my father's development of the X-ray spectrometer at Leeds, and I think one can trace the reason why crystal analysis was more rapidly developed in this country although it had started in Germany. My father was supreme at handling X-ray tubes and ionization chambers. You must find it hard to realize in these days what brutes X-ray tubes then were. One could not pass more than a milliampere through them for any length of time or the anticathodes got too hot. The discharge drove the gas into the walls; one then held a match under a little palladium tube which allowed some gas to diffuse through and so softened the tube. The measurement of ionization with a Wilson gold-leaf electroscope was quite an art too, and my father had thoroughly mastered all the techniques in his researches. The great strategical importance of the ionization spectrometer was that it enabled reflexions to be studied one by one. The discovery of three characteristic lines *A*, *B*, and *C* of platinum was announced in April 1913 and my establishment of the rocksalt structure enabled wavelengths to be assigned to these lines. It is not generally realized, I think, to what an extent my father founded the science of X-ray spectroscopy in 1913. He had tubes made with anticathodes of platinum, osmium, and iridium, of palladium and rhodium, and of copper and nickel. He found the wavelengths of their characteristic lines, and by measuring absorption coefficients he identified them as Barkla's *L* radiation in the platinum group of elements and *K* radiation in the other groups.

* *Early Days* is extracted, with permission, from *Proc. Roy. Soc.* (1961), A 262, 145. A few editorial changes have been made so that the extract reads smoothly where material has been omitted. *Manchester Days* (p. 173) has been specially written for the occasion.



*Yours very sincerely
W. L. Bragg*

Whiddington had established the energies of the cathode rays required to excite Barkla's *K* and *L* radiations in atoms of different atomic weight, so my father was able to link wavelength with energy and show that the relation was in agreement with Planck's quantum law. He found the *K* line pattern and the *L* line pattern to be similar for successive elements, and showed that the frequencies increased roughly as the square of the atomic weight (June 1913). He identified the absorption edges, as they are now termed. The link with Moseley's work is interesting. Moseley and Darwin had surveyed the spectrum emitted by a platinum anticathode, but missed the characteristic lines owing to setting their slits too fine. My father's success encouraged Moseley to review the lines for a continuous series of elements from aluminum to gold. Bohr was then at Manchester, and Moseley's triumph lay in explaining the succession of frequencies by Bohr's theory of spectra and so identifying the atomic number as the number of positive electronic charges on the nucleus (April 1914), in accord with the view put forward by van de Broek in the previous year that the charge carried by the nucleus is in all cases an integral multiple of the charge on the hydrogen nucleus.

I had the heaven-sent opportunity at this stage of joining in the work with the ionization spectrometer. My father was more interested in X-rays than in crystal structure, and I was able to use the spectrometer for investigating the latter. We published the diamond structure together, and I established the structures of ZnS, FeS₂, NaNO₃, and CaCO₃. The structure of pyrites, FeS₂, provided the greatest thrill. It seemed impossible to explain its queer succession of spectra until I discovered, going through Barlow's geometrical assemblages, that it was possible for a cubic crystal to have non-intersecting trigonal axes. The moment of realization that this explained the iron pyrites results was an occasion I well remember. I tried to explain it to an aunt who happened to be in the room, with indifferent success.

I will select three further papers which appeared during this period as standing out from the rest. The first was a paper by my father *The intensity of reflexion of X-rays by crystals*. He showed that one could get a quantitative measure of intensity of reflexion, which was not affected by variations of orientation of the blocks of an imperfect crystal, by sweeping the crystal at a uniform rate through the reflecting position. Comparing the reflexions from rocksalt with *h*, *k*, *l*, even, he found that the intensities fell on a single curve when plotted against $\sin \theta$. This sweep procedure was the start of accurate quantitative measurement, and is still the standard method. My father also measured the effect of temperature on the intensities, and found it to agree with Debye's formula for the reduction in intensity due to thermal vibration. The precision of the measurements would be considered quite respectable today, and is remarkable when one considers the X-ray equipment available at that time.

The second contribution was made by Darwin's two theoretical papers in 1914 on the intensity of X-ray reflexion. Darwin calculated that a perfect crystal should give complete reflexion over a range of a few seconds of arc. He realized that the actual reflexion was too strong to be accounted for in this way, correctly explained the discrepancy as being due to the crystal consisting of slightly disordered blocks, and obtained the formula for the mosaic crystal. They were remarkable papers. It was not till after the war that X-ray analysis reached a point where Darwin's results could be used; in fact Ewald then quite independently calculated the same formulae without realizing that Darwin had established the theory at the very start of X-ray analysis.

The third contribution appeared in my father's Bakerian Lecture (Bragg, W.H., 1915); a quotation from it will show its significance:

'Let us imagine then that the periodic variation of density (in the crystal) has been analysed into a series of periodic terms. The coefficient of any term will be proportional to the intensity of the reflexion to which it corresponds.'

It was the start of Fourier analysis, and my father used it to get some idea of the distribution of scattering matter in the atoms.

To sum up then the achievements of this first period from 1912 to 1920:

- (a) The wavelength of X-rays had been established.
- (b) A number of simple crystals had been analysed, including several with one parameter, and it had been shown that this parameter could be fixed with a high accuracy by comparing the orders of spectra. A parameter is a coordinate defining the position of an atom, which the crystal symmetry would permit to have any value.
- (c) A method for the accurate measurement of intensity had been found.
- (d) The Debye effect had been measured.
- (e) We had Darwin's formula for reflexion by perfect and mosaic crystals.
- (f) It had been realized that each crystal diffraction corresponds to a Fourier component of the density in the crystal.

(g) Finally, a whole new range of crystalline substances had become available through the powder method, developed in 1916 by Debye and Scherrer in Switzerland and independently a year later by Hull in America. In order to get a sufficient intensity, we used enormous crystals with the ionization spectrometer. We asked our colleagues to provide specimens an inch or two across if possible, though we had to be less ambitious in the case of diamond which fortunately had a low absorption coefficient and gave strong reflexions. The powder method opened the way to examining microcrystalline material.

How these achievements were applied when I became responsible for my own laboratory in Manchester are described in the following article.